

## SECTION 2. TERMOLECULAR REACTIONS

### Table of Contents

SECTION 2. TERMOLECULAR REACTIONS .....	2-1
2.1 Introduction.....	2-1
2.2 Low-Pressure-Limiting Rate Constant, $k_o^x(T)$ .....	2-2
2.3 Temperature Dependence of Low-Pressure Limiting Rate Constants: $T^n$ .....	2-2
2.4 High-Pressure-Limit Rate Constants, $k_\infty(T)$ .....	2-3
2.5 Temperature Dependence of High-Pressure-Limiting Rate Constants: $T^m$ .....	2-3
2.6 Uncertainty Estimates .....	2-3
2.7 Notes to Table 2.....	2-8
2.8 References .....	2-19

### Tables

Table 2-1. Rate Constants for Termolecular Reactions.....	2-2-4
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#### 2.1 Introduction

Rate constants for association reactions (Table 2) of the type  $A + B \leftrightarrow [AB]^* \xrightarrow{M} AB$  can be pressure dependent. The low-pressure-limiting rate constants are given in the form:

$$k_o(T) = k_o^{300} \left( \frac{T}{300} \right)^{-n} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

(where  $k_o^{300}$  has been adjusted for air as the third body). The limiting high-pressure rate constant is given in a similar form:

$$k_\infty(T) = k_\infty^{300} \left( \frac{T}{300} \right)^{-m} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

To obtain the effective second-order rate constant for a given condition of temperature and pressure (altitude), the following formula is used:

$$k_r([M], T) = \left( \frac{k_o(T)[M]}{1 + \frac{k_o(T)[M]}{k_\infty(T)}} \right) 0.6 \left\{ 1 + \left[ \log_{10} \left( \frac{k_o(T)[M]}{k_\infty(T)} \right) \right]^2 \right\}^{-1}$$

The fixed value 0.6 that appears in this formula fits the data for all listed reactions adequately, although in principle this quantity may be different for each reaction, and also temperature dependent.

Some reactions that appear to be simple bimolecular processes proceed via bound intermediates. The reaction between HO and CO to yield H + CO<sub>2</sub> takes place on a potential energy surface that contains the radical HOCO. The yield of H and CO<sub>2</sub> is diminished as the pressure rises. The loss of reactants is thus the sum of two processes, an association to yield HOCO and the chemical activation process yielding H and CO<sub>2</sub>. The total rate constant for loss of reactants is fit by the equation above for the association added to the chemical activation rate constant which can be represented by a similar looking equation:

$$k_r^{ca}([M],T) = \left( \frac{k_o(T)}{1 + \frac{k_o(T)}{k_\infty(T)/[M]}} \right) 0.6 \left\{ 1 + \left[ \log_{10} \left( \frac{k_o(T)}{k_\infty(T)/[M]} \right) \right]^2 \right\}^{-1}$$

Thus, a compilation of rate constants requires the stipulation of the four parameters,  $k_o(300)$ ,  $n$ ,  $k_\infty(300)$ , and  $m$ . These can be found in Table 2. The discussion that follows outlines the general methods we have used in establishing this table, and the notes to the table discuss specific data sources. Recent advances in theory have allowed direct calculation of rate constants for some reactions using RRKM/Master Equation methods.

When sufficient and precise data exist for a given reaction, we have fit the data to the four parameter expression above. We have used theory as a guide whenever possible.

## 2.2 Low-Pressure-Limiting Rate Constant, $k_o^x(T)$

Troe [324] has described a simple method for obtaining low-pressure-limiting rate constants. In essence this method depends on the definition:

$$k_o^x(T) \equiv \beta_x k_{o,sc}^x$$

Here  $sc$  signifies “strong” collisions,  $x$  denotes the bath gas, and  $\beta_x$  is an efficiency parameter ( $0 < \beta_x < 1$ ), which provides a measure of energy transfer. The strong collision rate constant can be calculated with some accuracy from knowledge of molecular parameters available from experiment and more and more from theory.

The coefficient  $\beta_x$  is related to the average energy transferred in a collision with gas  $x$ ,  $\langle \Delta E \rangle_x$ , via:

$$\frac{\beta_x}{(1 - \sqrt{\beta_x})} = \frac{\langle \Delta E \rangle_x}{F_E kT}$$

Notice that  $\langle \Delta E \rangle$  is quite sensitive to  $\beta$ .  $F_E$  is the correction factor of the energy dependence of the density of states (a quantity of the order of 1.1 for most species of stratospheric interest).

For some of the reactions of possible stratospheric interest reviewed here, there exist data in the low-pressure limit (or very close thereto), and we have chosen to evaluate and unify this data by calculating  $k_o^x(T)$  for the appropriate bath gas  $x$  and computing the value of  $\beta_x$  corresponding to the experimental value [324]. A compilation [265] gives details for many of the reactions considered here.

From the  $\beta_x$  values (most of which are for  $N_2$ , i.e.,  $\beta_{N_2}$ ), we compute  $\langle \Delta E \rangle_x$  according to the above equation. Values of  $\langle \Delta E \rangle_{N_2}$  of approximately 0.3–1 kcal mole<sup>-1</sup> are generally expected. If multiple data exist, we average the values of  $\langle \Delta E \rangle_{N_2}$  and recommend a rate constant corresponding to the  $\beta_{N_2}$  computed in the equation above.

Master equation calculations allow direct calculation of low pressure rate constants and of  $\beta_x$ .

Where no data exist we have sometimes estimated the low-pressure rate constant by taking  $\beta_{N_2} = 0.3$  at  $T = 300$  K, a value based on those cases where data exist.

## 2.3 Temperature Dependence of Low-Pressure Limiting Rate Constants: $T^n$

The value of  $n$  recommended here comes from measurements or, in some cases, a calculation of  $\langle \Delta E \rangle_{N_2}$  from the data at 300 K, and a computation of  $\beta_{N_2}$  (200 K) assuming that  $\langle \Delta E \rangle_{N_2}$  is independent of temperature in this range. This  $\beta_{N_2}$  (200 K) value is combined with the computed value of  $k_o^{sc}$  (200 K) to give the expected value of the actual rate constant at 200 K. This latter, in combination with the value at 300 K, yields the value of  $n$ .

This procedure can be directly compared with measured values of  $k_o$  (200 K) when those exist. Unfortunately, very few values at 200 K are available. There are often temperature-dependent studies, but some

ambiguity exists when one attempts to extrapolate these down to 200 K. If data are to be extrapolated beyond the measured temperature range, a choice must be made as to the functional form of the temperature dependence.

There are two general ways of expressing the temperature dependence of rate constants. Either the Arrhenius expression

$$k_0(T) = A \exp(-E/RT)$$

or the form

$$k_0(T) = A' T^{-n}$$

is employed. Neither of these extrapolation techniques is soundly based, and since they often yield values that differ substantially, we have used the method above as the basis of our recommendations.

## 2.4 High-Pressure-Limit Rate Constants, $k_\infty(T)$

High-pressure rate constants can often be obtained experimentally, but those for the relatively small species of atmospheric importance usually reach the high-pressure limit at inaccessibly high pressures. This leaves two sources of these numbers, the first being estimates based upon theory, and the second being extrapolation of fall-off data up to higher pressures.

Stratospheric conditions generally render reactions of interest much closer to the low-pressure limit and thus are fairly insensitive to the high-pressure value. This means that while the extrapolation is long, and the value of  $k_\infty(T)$  is often not very accurate, a “reasonable guess” of  $k_\infty(T)$  will then suffice. In a few cases we have declined to guess since the low-pressure limit is effective over the entire range of stratospheric conditions.

## 2.5 Temperature Dependence of High-Pressure-Limiting Rate Constants: $T^m$

There are very few data upon which to base a recommendation for values of  $m$ . Values in Table 2 are often estimated, based on models for the transition state of bond-association reactions and whatever data are available. In general the temperature dependence of these rate constants is expected to be small.

## 2.6 Uncertainty Estimates

For three-body reactions (Table 2) uncertainties are assigned using a procedure that is analogous to that employed for bimolecular reactions in Table 1. Values of  $f(298\text{ K})$  are given for these rate constants at room temperature and assumed to be valid at all pressures. The additional uncertainty arising from the temperature extrapolation has in previous evaluations been expressed as an uncertainty in the temperature coefficients  $n$  and  $m$ . In this evaluation, the reactions have been re-evaluated and uncertainties expressed with a  $g$ -factor as in Table 1. Given that uncertainties for an expression with four parameters is expressed with only two parameters, a certain amount of arbitrariness is involved in their choice. In general we have tried to have the “two sigma” range incorporate most of the data.

**Table 2-1. Rate Constants for Termolecular Reactions**

Reaction	Low-Pressure Limit <sup>a</sup> $k_0(T) = k_0^{300} (T/300)^{-n}$		High-Pressure Limit <sup>b</sup> $k_\infty(T) = k_\infty^{300} (T/300)^{-m}$		f	g	Notes
	$k_0^{300}$	n	$k_\infty^{300}$	m			
<b>O<sub>x</sub> Reactions</b>							
$O + O_2 \xrightarrow{M} O_3$	(6.0) (-34)	2.4	-	-	1.1	50	<a href="#">A1</a>
<b>O(<sup>1</sup>D) Reactions</b>							
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(2.8) (-36)	0.9	-	-	1.3	75	<a href="#">A2</a>
<b>HO<sub>x</sub> Reactions</b>							
$H + O_2 \xrightarrow{M} HO_2$	(4.4) (-32)	1.3	(4.7) (-11)	0.2	1.3	50	<a href="#">B1</a>
$OH + OH \xrightarrow{M} H_2O_2$	(6.9) (-31)	1.0	(2.6) (-11)	0	1.5	100	<a href="#">B2</a>
<b>NO<sub>x</sub> Reactions</b>							
$O + NO \xrightarrow{M} NO_2$	(9.0) (-32)	1.5	(3.0) (-11)	0.0	1.2	100	<a href="#">C1</a>
$O + NO_2 \xrightarrow{M} NO_3$	(2.5) (-31)	1.8	(2.2) (-11)	0.7	1.3	100	<a href="#">C2</a>
$OH + NO \xrightarrow{M} HONO$	(7.0) (-31)	2.6	(3.6) (-11)	0.1	1.2	50	<a href="#">C3</a>
$OH + NO_2 \xrightarrow{M} HONO_2$	(1.8) (-30)	3.0	(2.8) (-11)	0	1.3	100	<a href="#">C4</a>
$OH + NO_2 \xrightarrow{M} HOONO$	(9.1) (-32)	3.9	(4.2) (-11)	0.5	1.5	200	<a href="#">C4</a>
$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(2.0) (-31)	3.4	(2.9) (-12)	1.1	1.1	50	<a href="#">C5</a>
$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(2.0) (-30)	4.4	(1.4) (-12)	0.7	1.2	100	<a href="#">C6</a>
$NO_3 \xrightarrow{M} NO + O_2$	See Note						<a href="#">C7</a>
<b>Hydrocarbon Reactions</b>							
$OH + CO \xrightarrow{M} HOCO$	(5.9) (-33)	1.4	(1.1) (-12)	-1.3	1.1	100	<a href="#">D1</a>
$OH + CO \xrightarrow{M} H + CO_2$ [See Note]	(1.5) (-13)	-0.6	(2.1) (9)	-6.1			
$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(4.0) (-31)	3.6	(1.2) (-12)	-1.1	1.1	50	<a href="#">D2</a>
$C_2H_5 + O_2 \xrightarrow{M} C_2H_5O_2$	(1.5) (-28)	3.0	(8.0) (-12)	0	1.2	50	<a href="#">D3</a>
$OH + C_2H_2 \xrightarrow{M} HOCHCH$	(5.5) (-30)	0.0	(8.3) (-13)	-2	1.1	50	<a href="#">D4</a>
$OH + C_2H_4 \xrightarrow{M} HOCH_2CH_2$	(1.0) (-28)	4.5	(8.8) (-12)	.85	1.2	50	<a href="#">D5</a>
$CH_3O + NO \xrightarrow{M} CH_3ONO$	(2.3) (-29)	2.8	(3.8) (-11)	0.6	1.3	100	<a href="#">D6</a>

Reaction	Low-Pressure Limit <sup>a</sup> $k_0(T) = k_0^{300} (T/300)^{-n}$		High-Pressure Limit <sup>b</sup> $k_\infty(T) = k_\infty^{300} (T/300)^{-m}$		f	g	Notes
	$k_0^{300}$	n	$k_\infty^{300}$	m			
$\text{CH}_3\text{O} + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_3\text{ONO}_2$	(5.3) (-29)	4.4	(1.9) (-11)	1.8	1.1	0	<a href="#">D7</a>
$\text{C}_2\text{H}_5\text{O} + \text{NO} \xrightarrow{\text{M}} \text{C}_2\text{H}_5\text{ONO}$	(2.8) (-27)	4.0	(5.0) (-11)	0.2	1.2	50	<a href="#">D8</a>
$\text{C}_2\text{H}_5\text{O} + \text{NO}_2 \xrightarrow{\text{M}} \text{C}_2\text{H}_5\text{ONO}_2$	(2.0) (-27)	4.0	(2.8) (-11)	1.0	1.1	100	<a href="#">D9</a>
$\text{CH}_3\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_3\text{O}_2\text{NO}_2$	(1.0) (-30)	4.8	(7.2) (-12)	2.1	1.5	100	<a href="#">D10</a>
$\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{C}_2\text{H}_5\text{O}_2\text{NO}_2$	(1.2) (-29)	4.0	(9.0) (-12)	0.0	1.3	50	<a href="#">D11</a>
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$	(9.7) (-29)	5.6	(9.3) (-12)	1.5	1.2	50	<a href="#">D12</a>
$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{O}_2\text{NO}_2$	(9.0) (-28)	8.9	(7.7) (-12)	0.2	2.0	100	<a href="#">D13</a>
$\text{CH}_3\text{C}(\text{O})\text{CH}_2 + \text{O}_2 \xrightarrow{\text{M}} \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$	See Note						<a href="#">D14</a>
<b>FO<sub>x</sub> Reactions</b>							
$\text{F} + \text{O}_2 \xrightarrow{\text{M}} \text{FO}_2$	(5.8) (-33)	1.7	(1) (-10)	0	1.3	100	<a href="#">E1</a>
$\text{F} + \text{NO} \xrightarrow{\text{M}} \text{FNO}$	(1.2) (-31)	0.5	(2.8) (-10)	0	1.4	200	<a href="#">E2</a>
$\text{F} + \text{NO}_2 \xrightarrow{\text{M}} \text{FNO}_2$	(1.5) (-30)	2.0	(1.0) (-11)	0.0	1.3	100	<a href="#">E3</a>
$\text{FO} + \text{NO}_2 \xrightarrow{\text{M}} \text{FONO}_2$	(2.6) (-31)	1.3	(2.0) (-11)	1.5	3	200	<a href="#">E4</a>
$\text{CF}_3 + \text{O}_2 \xrightarrow{\text{M}} \text{CF}_3\text{O}_2$	(3.0) (-29)	4.0	(3.0) (-12)	1.0	1.2	100	<a href="#">E5</a>
$\text{CF}_3\text{O} + \text{NO}_2 \xrightarrow{\text{M}} \text{CF}_3\text{ONO}_2$	1.7 (-28)	6.9	1.1 (-11)	1	1.1	50	<a href="#">E6</a>
$\text{CF}_3\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CF}_3\text{O}_2\text{NO}_2$	(1.5) (-29)	2.2	(9.6) (-12)	1	1.1	50	<a href="#">E7</a>
$\text{CF}_3\text{O} + \text{CO} \xrightarrow{\text{M}} \text{CF}_3\text{OCO}$	(2.5) (-31)	2	(6.8) (-14)	-1.2	1.2	500	<a href="#">E8</a>
$\text{CF}_3\text{O} \xrightarrow{\text{M}} \text{CF}_2\text{O} + \text{F}$	See Note						<a href="#">E9</a>
<b>ClO<sub>x</sub> Reactions</b>							
$\text{Cl} + \text{O}_2 \xrightarrow{\text{M}} \text{ClOO}$	(2.2) (-33)	3.1	(1.8) (-10)	0	1.1	50	<a href="#">F1</a>
$\text{Cl} + \text{NO} \xrightarrow{\text{M}} \text{ClNO}$	(7.6) (-32)	1.8	-	-	1.2	50	<a href="#">F2</a>
$\text{Cl} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClONO}$ $\xrightarrow{\text{M}} \text{ClONO}_2$	(1.3) (-30)	2	(1) (-10)	1	1.2	100	<a href="#">F3</a>
	(1.8) (-31)	2	(1) (-10)	1	1.3	100	
$\text{Cl} + \text{CO} \xrightarrow{\text{M}} \text{ClCO}$	(1.3) (-33)	3.8	-	-	1.1	50	<a href="#">F4</a>
$\text{Cl} + \text{C}_2\text{H}_2 \xrightarrow{\text{M}} \text{ClC}_2\text{H}_2$	(5.2) (-30)	2.4	(2.2) (-10)	0.7	1.1	50	<a href="#">F5</a>
$\text{Cl} + \text{C}_2\text{H}_4 \xrightarrow{\text{M}} \text{ClC}_2\text{H}_4$	(1.6) (-29)	3.3	(3.1) (-10)	1.0	1.5	50	<a href="#">F6</a>

Reaction	Low-Pressure Limit <sup>a</sup> $k_0(T) = k_0^{300} (T/300)^{-n}$		High-Pressure Limit <sup>b</sup> $k_\infty(T) = k_\infty^{300} (T/300)^{-m}$		f	g	Notes
	$k_0^{300}$	n	$k_\infty^{300}$	m			
$\text{Cl} + \text{C}_2\text{Cl}_4 \xrightarrow{\text{M}} \text{C}_2\text{Cl}_5$	(1.4) (-28)	8.5	(4.0) (-11)	1.2	1.2	50	<a href="#">F7</a>
$\text{ClO} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClONO}_2$	(1.8) (-31)	3.4	(1.5) (-11)	1.9	1.3	50	<a href="#">F8</a>
$\text{OCIO} + \text{NO}_3 \xrightarrow{\text{M}} \text{O}_2\text{ClONO}_2$	See Note						<a href="#">F9</a>
$\text{ClO} + \text{ClO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_2$	(1.6) (-32)	4.5	(2.0) (-12)	2.4	1.1	25	<a href="#">F10</a>
$\text{ClO} + \text{OCIO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_3$	(6.2) (-32)	4.7	(2.4) (-11)	0	1.1	25	<a href="#">F11</a>
$\text{OCIO} + \text{O} \xrightarrow{\text{M}} \text{ClO}_3$	(2.9) (-31)	3.1	(8.3) (-12)	0	1.1	100	<a href="#">F12</a>
$\text{CH}_2\text{Cl} + \text{O}_2 \xrightarrow{\text{M}} \text{CH}_2\text{ClO}_2$	(1.9) (-30)	3.2	(2.9) (-12)	1.2	1.1	125	<a href="#">F13</a>
$\text{CHCl}_2 + \text{O}_2 \xrightarrow{\text{M}} \text{CHCl}_2\text{O}_2$	(1.3) (-30)	4.0	(2.8) (-12)	1.4	1.1	125	<a href="#">F14</a>
$\text{CCl}_3 + \text{O}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{O}_2$	(8) (-31)	6	(3.5) (-12)	1	1.2	50	<a href="#">F15</a>
$\text{CFCl}_2 + \text{O}_2 \xrightarrow{\text{M}} \text{CFCl}_2\text{O}_2$	(5.0) (-30)	4.0	(6.0) (-12)	1.0	1.3	200	<a href="#">F16</a>
$\text{CF}_2\text{Cl} + \text{O}_2 \xrightarrow{\text{M}} \text{CF}_2\text{ClO}_2$	(1.0) (-29)	4.0	(6) (-12)	1.0	2	300	<a href="#">F17</a>
$\text{CCl}_3\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{O}_2\text{NO}_2$	(2.9) (-29)	6.8	(1.3) (-11)	1	1.1	50	<a href="#">F18</a>
$\text{CFCl}_2\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CFCl}_2\text{O}_2\text{NO}_2$	(2.2) (-29)	5.8	(1.0) (-11)	1	1.1	50	<a href="#">F19</a>
$\text{CF}_2\text{ClO}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CF}_2\text{ClO}_2\text{NO}_2$	(1.1) (-29)	4.6	(1.7) (-11)	1.2	2	300	<a href="#">F20</a>
<b>BrO<sub>x</sub> Reactions</b>							
$\text{Br} + \text{NO}_2 \xrightarrow{\text{M}} \text{t-BrONO}$	(4.2) (-31)	2.4	(2.7) (-11)	0	1.1	50	<a href="#">G1</a>
$\text{BrO} + \text{NO}_2 \xrightarrow{\text{M}} \text{BrONO}_2$	(5.2) (-31)	3.2	(6.9) (-12)	2.9	1.2	400	<a href="#">G2</a>
<b>IO<sub>x</sub> Reactions</b>							
$\text{I} + \text{NO} \xrightarrow{\text{M}} \text{INO}$	(1.8) (-32)	1.0	(1.7) (-11)	0	1.3	150	<a href="#">H1</a>
$\text{I} + \text{NO}_2 \xrightarrow{\text{M}} \text{INO}_2$	(3.0) (-31)	1.0	(6.6) (-11)	0	1.5	300	<a href="#">H2</a>
$\text{IO} + \text{NO}_2 \xrightarrow{\text{M}} \text{IONO}_2$	(6.5) (-31)	3.5	(7.6) (-12)	1.5	1.3	50	<a href="#">H3</a>
<b>SO<sub>x</sub> Reactions</b>							
$\text{HS} + \text{NO} \xrightarrow{\text{M}} \text{HSNO}$	(2.4) (-31)	2.5	(2.7) (-11)	0	1.2	100	<a href="#">I1</a>
$\text{CH}_3\text{S} + \text{NO} \xrightarrow{\text{M}} \text{CH}_3\text{SNO}$	(3.2) (-29)	4.0	(3.5) (-11)	1.8	1.2	100	<a href="#">I2</a>
$\text{O} + \text{SO}_2 \xrightarrow{\text{M}} \text{SO}_3$	(1.8) (-33)	-2	4.2 (-14)	-1.8	2	100	<a href="#">I3</a>
$\text{OH} + \text{SO}_2 \xrightarrow{\text{M}} \text{HOSO}_2$	(3.3) (-31)	4.3	(1.6) (-12)		1.1	100	<a href="#">I4</a>

Reaction	Low-Pressure Limit <sup>a</sup> $k_0(T) = k_0^{300} (T/300)^{-n}$		High-Pressure Limit <sup>b</sup> $k_\infty(T) = k_\infty^{300} (T/300)^{-m}$		f	g	Notes
	$k_0^{300}$	n	$k_\infty^{300}$	m			
$\text{CH}_3\text{SCH}_2 + \text{O}_2 \xrightarrow{\text{M}} \text{CH}_3\text{SCH}_2\text{O}_2$	See Note						<a href="#">I5</a>
$\text{SO}_3 + \text{NH}_3 \xrightarrow{\text{M}} \text{H}_3\text{NSO}_3$	(3.6) (-30)	6.1	(4.3) (-11)	0	1.2	200	<a href="#">I6</a>
$\text{HO} + \text{CS}_2 \xrightarrow{\text{M}} \text{HO}\cdots\text{CS}_2$	(4.9) (-31)	3.5	(1.4) (-11)	1	1.5	100	<a href="#">I7</a>
$\text{Cl} + \text{CS}_2 \xrightarrow{\text{M}} \text{Cl}\cdots\text{CS}_2$	(5.9) (-31)	3.6	(4.6) (-10)	0	1.1	50	<a href="#">I8</a>
$\text{Cl} + (\text{CH}_3)_2\text{S} \xrightarrow{\text{M}} \text{Cl}\cdots(\text{CH}_3)_2\text{S}$	(4) (-28)	7	(2) (-10)	1	1.1	50	<a href="#">I9</a>
$\text{Br} + (\text{CH}_3)_2\text{S} \xrightarrow{\text{M}} \text{Br}\cdots(\text{CH}_3)_2\text{S}$	(3.7) (-29)	5.3	(1.5) (-10)	2	1.1	100	<a href="#">I10</a>
<b>Metal Reactions</b>							
$\text{Na} + \text{O}_2 \xrightarrow{\text{M}} \text{NaO}_2$	(3.2) (-30)	1.4	(6.0) (-10)	0	1.3	200	<a href="#">J1</a>
$\text{NaO} + \text{O}_2 \xrightarrow{\text{M}} \text{NaO}_3$	(3.5) (-30)	2.0	(5.7) (-10)	0	1.3	200	<a href="#">J2</a>
$\text{NaO} + \text{CO}_2 \xrightarrow{\text{M}} \text{NaCO}_3$	(8.7) (-28)	2.0	(6.5) (-10)	0	1.3	200	<a href="#">J3</a>
$\text{NaOH} + \text{CO}_2 \xrightarrow{\text{M}} \text{NaHCO}_3$	(1.3) (-28)	2.0	(6.8) (-10)	0	1.3	200	<a href="#">J4</a>

Shaded areas indicate changes or additions since JPL 02-25.

The values quoted are suitable for air as the third body, M.

a Units are  $\text{cm}^6/\text{molecule}^2\text{-s}$ .

b Units are  $\text{cm}^3/\text{molecule-s}$ .

$f(298 \text{ K})$  is the uncertainty factor at 298 K. To calculate the uncertainty at other temperatures, use the expression:

$$f(T) = f(298) \exp \left[ g \left( \frac{1}{T} - \frac{1}{298} \right) \right]$$

Note that the exponent is absolute value

## 2.7 Notes to Table 2

JPL Publication numbers for the most recent revision of the table entry and note are given at the end of each note.

- A1. O + O<sub>2</sub>. Low pressure limit and T dependence are an average of Klais et al. [180], Huie et al. [156] and Lin and Leu [205]. These studies in N<sub>2</sub> and Ar are in the temperature range (200<T/K<268). The result is in agreement with the study of Hippler et al. [146] and the extrapolated recommendation fits their lower pressure N<sub>2</sub> data down to 100 K. High pressure studies by Croce de Cobos and Troe [84] are in agreement with this recommendation. Rawlins et al. [280] estimate values in Ar between 80 and 150 K from nascent vibrational distributions that are a factor of two higher than the recommendation extrapolated to 80 K. The temperature dependence of the rate constant determined from the experimental data is in excellent agreement with the value of n=2.36 determined from the calculations of Patrick and Golden [265].

Kaye [174] has calculated isotope effects for this reaction, using methods similar to those discussed in the Introduction of this document (see Troe [324] and Patrick and Golden [265].) Isotope effects have been reported by Anderson et al. [9] and Gross and Billing [137]. Measurements of isotopic fractionation by Mauersberger and colleagues [360] and Thiemens and co-workers [294] reveal distinctly non-statistical effects. Various attempts at theoretical explanations exist [141], but the detailed knowledge of the potential energy surface required is unavailable. (Table: 02-25, Note: 02-25) [Back to table](#)

- A2. O(<sup>1</sup>D) + N<sub>2</sub>. Recommended parameters (including f and g) from Estupiñán et al. [109] whose detection capabilities were more advanced than those employed in earlier studies. Kajimoto and Cvetanovic [173] report a value at 296K of  $6.5 \times 10^{-37} \text{ cm}^6 \text{ s}^{-1}$ . Maric and Burrows [213] extract  $(8.8 \pm 3.3) \times 10^{-37} \text{ cm}^6 \text{ s}^{-1}$  from a study of the photolysis of synthetic air. Gaedtke et al. [128] report an approximate value of  $10^{12}$  in molar units, which translates to  $2.8 \times 10^{-36}$  in molecular units. The rate constant is extremely low in this special system due to electronic curve crossing. (Table: 06-2, Note: 06-2) [Back to table](#)

- B1. H + O<sub>2</sub>. Studies by Kurylo [186], Wong and Davis [362], Hsu et al. [155], Hsu et al. [154], Cobos et al. [70], Pirraglia et al. [271], Carleton et al. [60], Troe [325], Bates et al. [25] and Michael et al. [223] have been considered. All are in good agreement. The parameters in [25] are the basis for the recommendation. Several studies, [25, 223] have pointed out the large effect of water vapor as the collider gas. (Table: 06-2, Note: 06-2) [Back to table](#)

- B2. OH + OH. Recommended values are from fits of measurements by Zellner et al. [369] in N<sub>2</sub>, by Forster et al. [118] and Fulle et al. [126] in 1–150 bar He scaled to N<sub>2</sub>. A study by Fagerstrom et al. [110] in 85–1000 mbar SF<sub>6</sub> gives slightly different values. A pressure independent bimolecular channel to H<sub>2</sub>O + O with a rate  $4.2 \times 10^{-12} \exp(-240/T)$  is observed (see Table 1). Zellner et al. used somewhat different values for this rate constant to make substantial corrections to their measured values. Changing to the accepted value will make large changes in the Zellner et al. values and it is unclear how to evaluate this. Trainor and von Rosenberg [323] report a value at 300 K that is lower than recommended by a factor of 2.7. (Table: 02-25, Note: 02-25) [Back to table](#)

- C1. O + NO. Low pressure limit and n from direct measurements of Schieferstein et al. [295] and their re-analysis of the data of Whytock et al. [355]. Error limits encompass other studies. High pressure limit and m from fitting the data of Hippler et al. [147], who report higher values for the high pressure limiting rate constant, to the format used in this compilation. Shock tube measurements by Yarwood et al. [365] in argon from 300–1300 K are consistent with the values in Table 2. (Table: 06-2, Note: 06-2) [Back to table](#)

- C2. O + NO<sub>2</sub>. Values of rate constants and temperature dependences from a combination of the study by Burkholder and Ravishankara [50] and that of Hahn et al. [138]. At 300 K these studies almost overlap at the highest pressure of Burkholder and Ravishankara and the lowest pressure studied by Hahn et al. The former values are larger by a factor of 2.2 under these conditions. This recommendation is in reasonable agreement with the evaluation of Baulch et al. [27], which fits the Hahn et al. values very well. (Table: 02-25, Note: 02-25) [Back to table](#)

- C3. OH + NO. The low pressure limit rate constant has been reported by Anderson and Kaufman [7], Stuhl and Niki [319], Morley and Smith [230], Westenberg and de Haas [354], Anderson et al. [8], Howard and Evenson [153], Harris and Wayne [140], Atkinson et al. [17], Overend et al. [252], Anastasi and Smith [6], Burrows et al. [52] and Atkinson and Smith [12]. The general agreement is good, and the recommended values of both the rate constant and the temperature dependence are weighted averages. Studies by Sharkey et al. [304] and Donahue et al. [103] in the transition regime between low and high pressure limits are in agreement and serve to reduce the uncertainty. These latter studies yield a value for the high pressure limiting rate constant in agreement with the results of Forster et al. [118], whose study reached pressures of 100 bar in He. The temperature dependence of the high pressure limiting rate constant is from the data of Anastasi and Smith [6]



and Sharkey et al. (Both cis- and trans-HONO are expected to be formed.) Fulle et al. [127] report a high pressure limit in agreement with Forster et al. [118]. Pagsberg et al. [253] report low pressure values in SF<sub>6</sub> that are compatible (i.e. the ratio of collision efficiencies is about a factor of two.) with the recommendation. A study by Zabarnick [366] is noted. The error limits encompass the differences with the IUPAC [15] recommendation. (Table: 06-2, Note: 06-2) [Back to table](#)

- C4. OH + NO<sub>2</sub>. This reaction has been the subject of detailed study. There are two product channels, one to HONO<sub>2</sub> (nitric acid) and the other to HOONO (pernitrous acid). (There are at least two conformers of HOONO, cis-cis and trans-perp, but they are thought to be equilibrated under atmospheric conditions.) Golden and Smith [133] concluded that there were two pathways and they offered parameters in the format of this recommendation that were given in the note in JPL 02-25 [289]. Experiments by Hippler and co-workers [118, 127] up to about 100 bar at 300 K and the finding of a double exponential decay of OH at 430 K and 100 bar implicate a second pathway [145]. Nizkorodov and Wennberg [243] report 5% HOONO at 253K and 20 Torr of an N<sub>2</sub>/He buffer gas. Bean et al. [28] and Pollack et al. [274] report on the spectroscopy of the HOONO conformer. Donahue et al. [102] support the finding of two pathways in an analysis of isotopic effects. Golden et al. [132] have performed RRKM/master-equation calculations on a new ab initio surface to yield the parameters recommended herein. The low pressure limit and the high pressure limiting rate constants and their temperature dependences are from a fit to the data of Hippler et al. [145], Anastasi and Smith [5], Wine et al. [357], Donahue et al. [103], Dransfield et al. [104], Brown et al. [45] and D'Ottone et al. [85]. (Brown et al. report that O<sub>2</sub> is about 30% less efficient than N<sub>2</sub> as a collider and suggest that air might therefore have a total efficiency of 0.94 relative to N<sub>2</sub>) Data from Anderson et al. [8], Howard and Evenson [153], Burrows et al. [52], and Erler et al. [108] are in essential agreement. Data of Forster et al [118] and Fulle et al. [127] are acknowledged to be about 30% too high [145]. Burkholder et al. [48] and Dransfield et al. [104] have searched for the isomer HOONO and have been unable to identify it. The description of the reaction between HO and NO<sub>2</sub>, as consisting of two product channels, requires that the data obtained at lower than 300 K represent the sum of the two pathways. Thus the fate of HOONO has to be included in atmospheric models. If this fate involves rapid loss due to reaction or photolysis, the effect of the second pathway is the diminution of the HONO<sub>2</sub> forming rate constant. Evaluation of data, taking into account both pathways, indicates that the contribution of the HOONO forming reaction can be from 5 to 15% under atmospheric conditions. The equilibrium constant is given in Table 3-1. (Table: 06-2, Note: 06-2) [Back to table](#)
- C5. HO<sub>2</sub> + NO<sub>2</sub>. Christensen et al. [66] report rate constants 219 < T/K < 298 and 45 < P/torr < 200. They show that methanol, present in most other studies confounds the results by forming bound complexes with HO<sub>2</sub>. They also suggest that some measurements yielded low rate constants as a result of perturbations to the NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> equilibrium. The parameters recommended are those from this study incorporating the results of Kurylo and Ouellette [187, 188] and Sander and Peterson [291]. The recommended k<sub>0</sub> (300 K) is consistent with Howard [152]. Other studies by Simonaitis and Heicklen [308] and Cox and Patrick [82] are in reasonable agreement with the recommendation, as is the value of Christensen et al. [67]. (Table: 06-2, Note: 06-2) [Back to table](#)
- C6. NO<sub>2</sub> + NO<sub>3</sub>. Data with N<sub>2</sub> as the bath gas from Kircher et al. [178], Smith et al. [311], Burrows et al. [51], Wallington et al. [342] and Orlando et al. [249] ranging from 236 to 358 K were used to obtain k<sub>0</sub>, k<sub>∞</sub>, n and m. Values from Croce de Cobos et al. [83] are excluded due to arguments given by Orlando et al. [249], who point out that a reanalysis of these data using better values for the rate constant for NO<sub>3</sub> + NO → 2NO<sub>2</sub> yields a negative value for NO<sub>2</sub> + NO<sub>3</sub> + M. The study of Fowles et al. [120] is noted, but not used. Johnston et al. [163] have reviewed this reaction. Hahn et al. [138] have studied this reaction between 300 and 400 K at pressures from 30 to 900 bar. Their suggested parameterization yields values indistinguishable from those in this recommendation under most atmospheric conditions. (There are deviations of 30 to 50% at pressures less than a mbar and greater than 5 bar.)

A study of the reverse reaction has been carried out by Cantrell et al. [55]. These data are in excellent agreement with those obtained by Connell and Johnston [73] and Viggiano et al. [335]. The equilibrium constant recommended in Table 3 is the one given in Cantrell et al. [55], who computed it from the ratio of the rate constant of Orlando et al [249] and their rate constants for the reverse reaction. (Table: 02-25, Note: 02-25) [Back to table](#)

- C7. NO<sub>3</sub> + M. Johnston et al. [163] and Davidson et al. [91] have suggested significant thermal decomposition of NO<sub>3</sub>. This has been disputed by Russell et al. [285]. Davis et al. [93] claim that the barrier to thermal dissociation is 47.3 kcal mol<sup>-1</sup>. This would seem to rule out such a process in the atmosphere. (Table: 94-26, Note: 94-26) [Back to table](#)
- D1. HO + CO. This recommendation takes into account the fact that the reaction proceeds via two channels, a chemical activation process directly to H + CO<sub>2</sub> and an association to yield HOCO. In the presence of O<sub>2</sub>, the HOCO intermediate is converted to HO<sub>2</sub> + CO<sub>2</sub> (DeMore [95], Miyoshi et al. [227]). Miyoshi et al. report a

rate constant for the reaction of HOCO with O<sub>2</sub> of  $\sim 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K)). Therefore, for atmospheric purposes, the products can be taken to be HO<sub>2</sub> and CO<sub>2</sub>. The parameters are taken directly from Senosiain et al. [301] who performed master equation calculations on a theoretical surface. Pressure and temperature dependence of data from McCabe et al. [219] and Hynes et al. [158] are well represented by these parameters. In contrast with the previous evaluation where the rate constant increased with pressure, in this evaluation, it is shown to increase with number density. This reaction has been studied often by many workers. In general the results are in keeping with the current recommendation. Values have been reported by Dreier and Wolfrum [105], Husain et al. [157], Ravishankara and Thompson [279], Paraskevopoulos and Irwin [259], Hofzumahaus and Stuhl [149]. The results of Jonah et al. [165] are too high and were not included. An increase in k with pressure has been observed by a large number of investigators (Overend and Paraskevopoulos [251], Perry et al. [268], Chan et al. [61], Biermann et al. [31], Cox et al. [78], Butler et al. [53], Paraskevop and Irwin [258, 259], DeMore [95], Hofzumahaus and Stuhl [149], Hynes et al. [158]), and McCabe et al., [219]. In addition, Niki et al. [242] have measured k relative to OH + C<sub>2</sub>H<sub>4</sub> in one atmosphere of air by following CO<sub>2</sub> production using FTIR. Previous controversy regarding the effect of small amounts of O<sub>2</sub> (Biermann et al. [31]) has been resolved and is attributed to secondary reactions (DeMore [95], Hofzumahaus and Stuhl [149]). The results of Butler et al. [53] have to be re-evaluated in the light of refinements in the rate coefficient for the OH + H<sub>2</sub>O<sub>2</sub> reaction. The corrected rate coefficient is in approximate agreement with the recommended value. Currently, there are no indications to suggest that the presence of O<sub>2</sub> has any effect on the rate coefficient other than as a third body. Beno et al. [30] observe an enhancement of k with water vapor, which is in conflict with the flash photolysis studies; e.g., Ravishankara and Thompson [279], Paraskevopoulos and Irwin [259], Hynes et al. [158], and McCabe et al. [219]. Water is not expected to significantly change the rate coefficient for the reaction in the atmosphere and it is not expected to alter the products of the reaction.

**Important:** To calculate rate constants for the reaction  $\text{OH} + \text{CO} \xrightarrow{\text{M}} \text{HOCO}$ , use the standard expression for termolecular reactions,  $k_f([\text{M}], T)$ , given in the Introduction (section 2.1). The Arrhenius parameters for the reaction  $\text{HOCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}_2$  are given in Table 1-1. To calculate rate constants for the reaction  $\text{OH} + \text{CO} \xrightarrow{\text{M}} \text{H} + \text{CO}_2$ , use the expression for chemical activation reactions,  $k_f^{\text{ca}}([\text{M}], T)$ , given in the Introduction (section 2.1). (Table: 06-2, Note: 06-2) [Back to table](#)

- D2. CH<sub>3</sub> + O<sub>2</sub>. *The temperature dependence of the high pressure limit is positive. There has been a sign error in the last several versions of this recommendation!* Data from Kaiser [168] are fit to the NASA format. This ranges of this study were  $3 < P/\text{torr} < 11000$  and  $264 < T/\text{K} < 370$ . The rate constant was measured relative to the reaction  $\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}$ . [ $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = 1.61\text{E}-12 \exp(-530/RT)$ ] The recommended values are in good agreement with those from Selzer and Bayes [300]. These workers determined the rate constants as a function of pressure in N<sub>2</sub>, Ar, O<sub>2</sub>, and He. Plumb and Ryan [273] report a value in He which is consistent within error limits with the work of Selzer and Bayes. Pilling and Smith [270] have measured this process in Ar (32–490 Torr). Cobos et al. [69] have made measurements in Ar and N<sub>2</sub> from 0.25 to 150 atmospheres. They report parameters somewhat different than recommended here. The work of Laguna and Baughcum [189] seems to be in the fall-off region. Results of Pratt and Wood [276] in Ar are consistent with this recommendation, although the measurements are indirect. The suggested value accommodates the values of Keiffer et al., [175], who measured the process in Ar between 20 and 600 Torr and in the range  $334 < T/\text{K} < 582$ . Data of van den Bergh and Callear [334], Hohanadel et al. [148], Basco et al. [24], Washida and Bayes [353], Laufer and Bass [192], and Washida [352] are also considered. A theoretical study by Zhu et al. [372] is in reasonable agreement with the recommendation. (Table: 06-2, Note: 06-2) [Back to table](#)
- D3. C<sub>2</sub>H<sub>5</sub> + O<sub>2</sub>. Kaiser et al. [171] extract from a relative rate study:  $k_{\infty} = (9.2 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_0 = (6.5 \pm 2.0) \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  in He at 298 K and pressures between 3 and 1500 Torr.  $k_{\infty}$  has been calculated by Wagner et al. [338], Miller and Klippenstein [225], and Sheng et al. [306] with  $k_{\infty}(300\text{K}) = 8, 10, \text{ and } 4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. Although all cite some small temperature dependence, the values are stated to hold above 300K. The Kaiser et al. [171], extrapolation to the low-pressure limit is difficult due to the complex potential energy surface, but agrees with a Patrick and Golden-type calculation [265] using  $\Delta H_0^{\circ} = 32.4 \text{ kcal mol}^{-1}$ . The recommended values use the calculated temperature dependence and a 2.5 times higher rate constant for air as the bath gas, in line with suggestions in Kaiser et al. [169]. (Table: 06-2, Note: 06-2) [Back to table](#)
- D4. OH + C<sub>2</sub>H<sub>2</sub>. The rate constant for this complex process has been examined by Smith et al. [312] in the temperature range from 228 to 1400 K, and in the pressure range 1 to 760 Torr. Their analysis, which is cast in similar terms to those used here, is the source of the rate constants and temperature dependences at both limits.

The negative value of  $m$  reflects the fact that their analysis includes a 1.2 kcal/mol barrier for the addition of OH to  $C_2H_2$ . The data analyzed include those of Pastrana and Carr [264], Perry et al. [268], Michael et al. [224], and Perry and Williamson [269]. Other data of Wilson and Westenberg [356], Breen and Glass [40], Smith and Zellner [315], and Davis et al. [92] were not included. Studies by Liu et al. [206] and Lai et al. [190] are in general agreement with the recommendation. Calculations of  $k_0$  via the methods of Patrick and Golden [265] yield values compatible with those of Smith et al. [312]. A study by Sørensen et al. [316] at 298 K and pressures from 25 to 8000 torr of bath gas suggests  $k_0/cm^6 molecule^{-2} s^{-1} = 2.92E-30$ ,  $k_c/cm^3 molecule^{-1} s^{-1} = 9.69E-13$  and  $F_c = 0.6$ . No difference was found between air,  $N_2/O_2$  mixtures or  $O_2$  as the bath gas. These values yield rate constants as a function of pressure at 298K in agreement with this recommendation, so the recommended values are unchanged from JPL 02-25. Earlier, Fulle et al. [125] reported a high pressure limiting rate constant of  $2E-12 cm^3 molecule^{-1} s^{-1}$ , which is the basis for the IUPAC [15] recommendation. A theoretical study by Senosiain et al. [302] is in essential agreement with this recommendation. (Table: 06-2, Note: 06-2) [Back to table](#)

- D5.  $OH + C_2H_4$ . A study by Vakhtin et al. [331] at 296K in  $N_2$  between  $2.85 \times 10^{16}$  and  $3.25 \times 10^{18}$  molecules  $cm^{-3}$  and individual points 96K,  $1.9 \times 10^{16}$  molecules  $cm^{-3}$ ; 110K,  $2.65 \times 10^{16}$  molecules  $cm^{-3}$ ; and 165K and  $3.5 \times 10^{16}$  molecules  $cm^{-3}$ , as well as data of Tully [328], Davis et al. [92], Howard [151], Greiner [135], Morris et al. [231], and Overend and Paraskevopoulos [250] in helium, Atkinson et al. [12] in argon, and Lloyd et al. [207] and Cox [75] and Klein et al. [181] in nitrogen/oxygen mixtures, have been considered in the evaluation. This well-studied reaction is considerably more complex than most others in this table. The parameters recommended here fit the same curve proposed by Klein et al. [181] at 298 K. Kuo and Lee [185] report very strong temperature dependence for the low-pressure limit ( $n=4$ ). Calculations of the type in Patrick and Golden [265] as described in Vakhtin et al. [331] yield  $n = 4.2$ , although they use a somewhat low value for energy transfer by nitrogen. The high-pressure limit temperature dependence has been determined by several workers. Zellner and Lorenz [370] report a value equivalent to  $m = +0.8$  over the range ( $296 < T/K < 524$ ) at about 1 atmosphere. A value of  $m = +2.0$  fits the data ( $540 < T/K < 670$ ) of Diau and Lee [98]. (Table: 06-2, Note: 06-2) [Back to table](#)
- D6.  $CH_3O + NO$ . This reaction proceeds via a complex potential energy surface that includes both chemical activation and direct abstraction routes [59] to the disproportionation products  $CH_2O$  and  $HNO$  as well as the combination to form  $CH_3NO$ . The chemical activation process would have inverse pressure dependence and the direct abstraction would be pressure independent. The recommended values take into account the results of Frost and Smith [123] in Ar and  $CF_4$  and of Caralp et al. [59] in He and Ar. In both of these references the disproportionation process is subtracted from total loss of  $CH_3O$  with a pressure independent, temperature dependent value. At 300K below one torr the disproportionation process dominates. Temperature dependences are from the higher temperature results. The low pressure rate constant is consistent with the measurements of McCaulley et al. [221] and Daële et al. [86] in helium. Studies by Ohmori et al. [245] and Dobé et al. [101] are in general agreement with respect to both the addition and bimolecular pathways. (See the note in Table 1-1 for the bimolecular pathway.) (Table: 06-2, Note: 06-2) [Back to table](#)
- D7.  $CH_3O + NO_2$ . The recommended values are from the work mostly in Ar of Wollenhaupt and Crowley [361]. Agreement is good with earlier work at 298 K from the study of Frost and Smith [122] in Ar (corrected by Frost and Smith [124] and that of Biggs et al [32] and Martinez et al. [217] in He. Low pressure results agree within a factor of two with the measurements of McCaulley et al. [220] in He. A minor bimolecular (chemical activation) pathway is also observed. (See Table 1-1.) (Table: 02-25, Note: 06-2) [Back to table](#)
- D8.  $C_2H_5O + NO$ . High-pressure data at 298 K in Ar from Frost and Smith [123] and in He between 286 and 388K at pressures from 30 to 500 torr, from Fitschen et al. [114]. Low-pressure measurements in He are from Daele et al. [87]. He experiments were scaled to  $N_2$  by dividing by a factor of 2.5. Ar data were taken as equivalent to  $N_2$  or air. The data were fit by subtracting an assumed pressure independent value of  $1E-11$  from the measured rate constants to account for the route to form  $HNO$  and  $CH_3CHO$ . The low pressure value agrees with theory. The bimolecular channel with an estimated rate of about  $10^{-11}$  needs to be verified by direct studies. The temperature dependence of the low pressure limit is estimated and that of the high pressure limit is taken from Fitschen et al. [114]. (The high pressure rate expression in Fitschen et al. seems to be in error.) (Table: 06-2, Note: 06-2) [Back to table](#)
- D9.  $C_2H_5O + NO_2$ . High-pressure rate constant at 298 K from Frost and Smith [122]. Other values estimated from similar reactions. (Table: 06-2, Note: JPL92-20) [Back to table](#)
- D10.  $CH_3O_2 + NO_2$ . Golden [131] has re-evaluated the data for this reaction. The recommended parameters are from a fit to Percival [267] and temperature- and pressure-dependent data in Sander and Watson [293] and Ravishankara et al. [277]. The temperature dependence of the high pressure rate constant is a little high, but results from the statistical fit to the data. The values recommended herein, were taken with the data in a study

of the reverse reaction by Zabel et al. [367] to compute the value of the equilibrium constant in Table 3. Destriau and Troe [97] have fit the above data with  $k_{\infty}$  independent of temperature and  $F_c = 0.36$ . Bridier et al. [43] are in good agreement with this recommendation at one atmosphere and 298 K. (Table: 06-2, Note: 06-2) [Back to table](#)

- D11.  $C_2H_5O_2 + NO_2$ . The only experimental study is that of Elfers et al. [106] who measured the rate constant relative to the  $C_2H_5O_2 + NO$  reaction between 10 and 1000 mbar. Elfers et al. used a value of  $k = 8.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reference reaction. By comparison the recommended rate constant for the reference reaction from Table 1-1 of this evaluation is  $1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 254 K. There are three data points. An evaluation of the Elfers et al. work by Destriau and Troe [97] cast the data in the format used in the IUPAC evaluation [16]. The parameters in Table 2 are adjusted to agree with the data corrected for the change in the reference reaction, using the simpler formula employed in this recommendation. (Table: 02-25, Note: 02-25) [Back to table](#)
- D12.  $CH_3C(O)O_2 + NO_2$ . The recommended parameters are from the data of Bridier et al. [42], who report in the format represented here, but using  $F_c = 0.3$ . Their values are:  $k_0^{300} = (2.7 \pm 1.5) \times 10^{-28}$ ,  $k_{\infty}^{300} = (12.1 \pm 2.0) \times 10^{-12}$ , with  $n = 7.1 \pm 1.7$  and  $m = 0.9 \pm 0.15$ . Studies of the decomposition of  $CH_3C(O)O_2NO_2$  [PAN] by Roberts and Bertman [284], Grosjean et al. [136], and Orlando et al. [248] are in accord with those of Bridier et al. [42]. In the Roberts and Bertman [284] study it was shown that PAN decomposition yields only peroxyacetyl radical and  $NO_2$ ; no methyl nitrate. Studies by Seefeld et al. [297] and Sehested et al. [299] of the relative rates of  $CH_3C(O)O_2$  with  $NO$  and  $NO_2$  are confirmatory. A study by von Ahsen et al. [337] involving matrix isolation of the products of PAN decomposition, suggests a minor pathway due to O-O bond fission. (Table: 06-2, Note: 06-2) [Back to table](#)
- D13.  $CH_3CH_2C(O)O_2 + NO_2$ . This reaction, forming peroxypropionyl nitrate (PPN), has been studied in the reverse direction by Schurath and Wipprecht [296], Mineshos and Glavas [226], Grosjean et al. [136] and Kirchner et al. [179]. Group additivity considerations indicate that the equilibrium constant for both PAN and PPN will be the same (both sides of the equilibrium for PPN differ from those for PAN by the group C-(C)(CO)(H)<sub>2</sub>.) Therefore, the recommended value for the association reaction is taken from the decomposition studies multiplied by the same equilibrium constant as for PAN. The resulting values are very similar to those for  $CH_3C(O)O_2 + NO_2$  forming peroxyacetyl nitrate (PAN). Conservative error limits are estimated. (Table: 02-25, Note: 06-2) [Back to table](#)
- D14.  $CH_3C(O)CH_2 + O_2$ . Cox et al. [81] reported a value of  $k = (1.5 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and 1 atm of  $SF_6$  in which a pulse radiolysis study was modeled. This should be close to the high-pressure limit, but Cox et al point out that it is a bit low. (Using group additivity to calculate the entropy change yields about  $10^{14.3} \text{ s}^{-1}$  for the decomposition A-factor. This compares with almost  $10^{15} \text{ s}^{-1}$  for  $C_2H_5O_2$  decomposition.) (Table: 02-25, Note: 02-25) [Back to table](#)
- E1.  $F + O_2$ . Values are taken from a study by Campuzano-Jost et al. [54], with experiments from 100 to 420K at pressures of He, Ar and  $N_2$  from 1 to 1000 bar. (They used  $F_c = 0.54(T/300)^{0.09}$ , but the results are essentially the same with  $F_c = 0.6$ .) A study by Pagsberg et al. [257] reports  $k_0$  in argon =  $4.38 \times 10^{-33} (T/300)^{-1.2}$ . There is also good agreement with earlier values of Smith and Wrigley [313], Smith and Wrigley [314], Shamonina and Kotov [303], Arutyunov et al. [10], Wallington and Nielsen [348], Wallington et al. [347] and Ellerman et al. [107]. The values are slightly lower than the values of Chen et al. [64] and Chegodaev et al. [63]. Lyman and Holland [211] report a slightly lower value in Ar at 298K. Campuzano-Jost et al. [54] and Pagsberg et al. [257], also determined the equilibrium constant and thus  $\Delta H_{f,298}(FO_2) = 6.13 \pm 0.5 \text{ kcal mol}^{-1}$ . See  $F + O_2$  in Table 3-1. (Table: 06-2, Note: 06-2) [Back to table](#)
- E2.  $F + NO$ . A study by Pagsberg et al [254], taking into account data from Zetzsch [371], Skolnik et al. [309], Kim et al. [177], Pagsberg et al. [256] and Wallington et al. [345], reports rate constants for this reaction in several bath gases. Re-evaluating the data and converting to the form used in this compilation yields the recommended parameters. (Table: 06-2, Note: 06-2) [Back to table](#)
- E3.  $F + NO_2$ . Fasano and Nogar [111] studied this reaction in  $N_2$  at 300K. Pagsberg et al. [255] studied the reaction in  $SF_6$  and Zetzsch [371] studied it in He. The results from Fasano and Nogar [111] and Pagsberg et al. [255] were used to determine both the high and low pressure limits at 300 K. Treatment of the data for this system requires knowledge of the relative stabilities of  $FNO_2$  and  $FONO$ . Patrick and Golden [265] assumed that the difference between these would be the same as between the  $CINO_2$  isomers. Theoretical work by Dixon and Christie [100], Lee and Rice [196] and Amos et al. [4] indicates that  $FNO_2$  is 35–40  $\text{kcal mol}^{-1}$  more stable than  $FONO$ , and therefore the measured rate refers to  $FNO_2$  formation. The value of  $n = 2$  is from Patrick and Golden, but consistent with Pagsberg et al. [255] who made a few measurements at 341K. The value of  $m$  is a

rough estimate from similar reactions, but is also consistent with Pagsberg et al. [255]. (Table: 06-2, Note: 06-2) [Back to table](#)

- E4. FO + NO<sub>2</sub>. Low pressure limit from strong collision calculation and  $\beta = 0.33$ . T dependence from resultant  $\langle \Delta E \rangle = 0.523 \text{ kcal mol}^{-1}$ , high-pressure limit and T dependence estimated. A theoretical study by Rayez and Destriau [281] indicates that the product is the single isomer FONO<sub>2</sub>. Bedzhanyan et al. [29] report a value extracted from a complex mixture of bath gases. (Table: 06-2, Note: 94-26) [Back to table](#)
- E5. CF<sub>3</sub> + O<sub>2</sub>. Caralp et al. [57] have measured the rate constant in N<sub>2</sub> between 1 and 10 Torr. This supersedes the value from Caralp and Lesclaux [56]. Kaiser et al. [172] have extended the pressure range to 580 Torr measuring the reaction relative to the reaction of CF<sub>3</sub> with Cl<sub>2</sub>. Breheny et al. [41] report values at 295 K from 2-110 torr and they make a cogent argument for lowering the value of the rate constant used by Kaiser et al for their reference reaction by about 50%. This has the effect of lowering the Kaiser values. Each study recommends different parameters, but the data are well represented by the currently recommended values. Data of Ryan and Plumb [287] are in general agreement. Forst and Caralp [116] have examined this reaction theoretically. (Table: 06-2, Note: 06-2) [Back to table](#)
- E6. CF<sub>3</sub>O + NO<sub>2</sub>. Fockenberget al. [115] report values in nitrogen with  $250 < T/K < 302$  and  $7 < p/\text{mbar} < 107$ . They report large error limits. Their values, including two sigma errors, using the previous format are:  $k_0 = (3.1 \pm 3.0) \times 10^{-28}$ ,  $n = (2.0 \pm 2.0)$ ;  $k_\infty = (1.5 \pm 0.5) \times 10^{-28}$ ,  $m = (2.8 \pm 2.0)$ . These were used in JPL 02-25. Here the data has been fit forcing  $m = 1$ , as values as large as  $m = 2.8$  are not justifiable. The reaction products agree with those reported by Chen et al. [65], who used photolysis of CF<sub>3</sub>NO to prepare CF<sub>3</sub>O<sub>2</sub> and subsequently CF<sub>3</sub>O in 700 Torr of air at  $297 \pm 2 \text{ K}$ . They considered two product channels: (a) CF<sub>3</sub>ONO<sub>2</sub> obtained via three-body recombination and (b) CF<sub>2</sub>O + FNO<sub>2</sub> obtained via fluorine transfer. Both products were observed and found to be thermally stable in their reactor. They report  $k_a/(k_a+k_b) > 90\%$  and  $k_b/(k_a+k_b) < 10\%$ , thus the formation of CF<sub>3</sub>ONO<sub>2</sub> is the dominant channel at 700 Torr and 297 K. (Table: 06-2, Note: 06-2) [Back to Table](#)
- E7. CF<sub>3</sub>O<sub>2</sub> + NO<sub>2</sub>. The data is from experiments in O<sub>2</sub> of Caralp et al. [58], who suggest a somewhat different fitting procedure than used here. A statistical best fit to the data yields a value of  $m = 5.7$ , but the values recommended here fit the data just about as well. Destriau and Troe [97] use yet a different fitting procedure that does not represent the data quite as well as that recommended here. Reverse rate data are given by Köppenkastrop and Zabel [183]. (Table: 06-2, Note: 06-2) [Back to table](#)
- E8. CF<sub>3</sub>O + CO. Values taken from Turnipseed et al. [329]. The numbers were obtained for Ar as the bath gas and are assumed to hold for N<sub>2</sub> as well. The temperature dependence of the high-pressure rate constant was determined over the range  $233 < T/K < 332$  in SF<sub>6</sub>. No temperature dependence of the low-pressure-limiting rate constant was reported. The value in the table is an estimate. Wallington and Ball [343] report values in good agreement with Turnipseed et al. [329]. (Table: 06-2, Note: 06-2) [Back to table](#)
- E9. CF<sub>3</sub>O + M. The activation energy for thermal decomposition of CF<sub>3</sub>O to CF<sub>2</sub>O + F has been reported to be  $31 \text{ kcal mol}^{-1}$  by Kennedy and Levy [176]. Thermochemical data yield  $\Delta H^0(298) = 23 \text{ kcal mol}^{-1}$ . This implies an intrinsic barrier of about  $8 \text{ kcal mol}^{-1}$  to elimination of F from CF<sub>3</sub>O. Electronic structure calculations by Li and Francisco [204] support this observation. Adopting the A-factor for unimolecular dissociation,  $A = 3 \times 10^{14} \text{ s}^{-1}$  and  $E = 31 \text{ kcal mol}^{-1}$  from Kennedy and Levy,  $k_\infty(298 \text{ K})$  is about  $6 \times 10^{-9} \text{ s}^{-1}$ . This corresponds to a lifetime of about 6 years; therefore, thermal decomposition of CF<sub>3</sub>O is unimportant throughout the atmosphere. (Table: 94-26, Note: 94-26) [Back to table](#)
- F1. Cl + O<sub>2</sub>. Nicovich et al. [237] measured the rate constant at  $181 < T/K < 200$  and  $15 < p/\text{torr} < 40$  in O<sub>2</sub>. They reported  $k_0 = (9 \pm 3) 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  at  $T = 187 \pm 6 \text{ K}$  in O<sub>2</sub>. The recommended low pressure limiting parameters are from fitting their data over the entire range and assuming the same value for N<sub>2</sub> as the bath gas. The value from the calculation at 300 K (i.e.,  $2.2 \times 10^{-33} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1}$ ) compares with an older value of Nicholas and Norrish [235] of  $1.7 \times 10^{-33}$  in an N<sub>2</sub> + O<sub>2</sub> mixture. Baer et al. [19] report a value in O<sub>2</sub> of  $k_0 = (1.6) 10^{-33} (T/300)^{-2.9} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  in good agreement with the value recommended here. They also report a value in N<sub>2</sub> of  $k_0 = (1.4) 10^{-33} (T/300)^{-3.9} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ . A theoretical study by Zhu and Lin [376] suggests  $k_0 = (1.26) 10^{-16} T^{6.22} \exp(-943/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  in O<sub>2</sub> ( $2.0 \times 10^{-33}$ ) at 300K with  $k_\infty = (1.8) 10^{-10} \text{ s}^{-1}$ , which is adopted here. The Nicovich et al [237] data is so far from the high pressure limit, that the difference in values for the high pressure rate constant can't be evaluated easily. Baer et al [19] suggest  $k_\infty = 2.7 \times 10^{-11} \text{ s}^{-1}$ , but the data suggest a higher value. (Table: 06-2, Note: 06-2) [Back to table](#)
- F2. Cl + NO. Low-pressure limit and temperature dependence is from re-evaluation of data from Lee et al. [194]. Clark et al. [68] and Ashmore and Spencer [11] also have data in agreement with the recommendation. (Table: 06-2, Note: 06-2) [Back to table](#)
- F3. Cl + NO<sub>2</sub>. Low-pressure limit at 300 K from Leu [202] and Ravishankara et al. [278]. The latter study extended the data to 200 Torr in He. A turbulent flow study by Seeley et al. [298] extended the results to 250

Torr of Ar and the high-pressure limit was chosen to fit these two studies after taking into account differences in collisional efficiencies of the bath gases. Leu [202] confirms the observation of Niki et al. [241] that both ClONO and ClNO<sub>2</sub> are formed, with the former dominating. This has been explained by Chang et al. [62], with detailed calculations in Patrick and Golden [265]. The temperature dependence is as predicted in Patrick and Golden [265] and is the same as Leu's results in He. Ravishankara et al. [278] report a few data points in N<sub>2</sub> that may suggest a somewhat higher temperature dependence. The temperature dependence of the high-pressure limit is estimated. The uncertainty limits are estimated. (Table: 06-2, Note: 06-2) [Back to table](#)

- F4. Cl + CO. From Nicovich et al. [238], who measured the process in N<sub>2</sub> for 185 ≤ T/K ≤ 260. Hewitt et al. [144] report a value at one atmosphere and 298 K with <sup>13</sup>CO in agreement with Nicovich et al. [238]. (Table: 06-2, Note: 06-2) [Back to table](#)
- F5. Cl + C<sub>2</sub>H<sub>2</sub>. The recommended values are a statistical fit to the work of Kaiser [167] in air. Kaiser and Wallington [166] extends the pressure range at 296K to 0.3–6000 Torr. The data are in reasonable agreement with earlier measurements of Brunning and Stief [46] and Wallington et al. [340], although the derived temperature dependence is less than obtained by Brunning and Stief [46]. These values are compatible with earlier studies of Poulet et al. [275], Atkinson and Aschmann [13], Lee and Rowland [193] and Wallington et al. [349]. Using FTIR, Zhu et al. [377] reported branching of 16% and 84% to the trans and cis adduct isomers, respectively, at 700 Torr N<sub>2</sub> and 295 K. (Table: 06-2, Note: 06-2) [Back to table](#)
- F6. Cl + C<sub>2</sub>H<sub>4</sub>. Values at 300 K are from a relative rate study by Wallington et al. [340]. A relative rate study by Kaiser and Wallington [166] extends the pressure range to 0.3–6000 Torr and is compatible with earlier studies. Temperature dependence of k<sub>0</sub> is taken from Kaiser and Wallington [170]. The temperature dependence of k<sub>∞</sub> is estimated. Values are in reasonable agreement with studies by Maricq et al. [214], Lee and Rowland [193], Iyer et al. [161], Atkinson and Aschmann [13], Atkinson and Aschmann [14] and Wallington et al. [350]. A study in He by Stutz et al. [320] is noted, as is a comment on it by Kaiser and Wallington [170]. Knyasev et al. [182] have done an extensive experimental and theoretical analysis. Their values agree with this recommendation. (Table: 97-4, Note: 02-25) [Back to table](#)
- F7. Cl + C<sub>2</sub>Cl<sub>4</sub>. Recommendation is from the flash-photolysis study of Nicovich et al. [240] done at 231–390 K in 3–700 Torr N<sub>2</sub>. A study by Thuner et al. [322] is in agreement. (Table: 97-4, Note: 02-25) [Back to table](#)
- F8. ClO + NO<sub>2</sub>. The low-pressure-limit recommendation and uncertainties are based on temperature-dependent values from Zahniser et al. [368], Lee et al. [198], Birks et al. [35], Leu et al. [202], Wallington and Cox [344], Cox et al. [76] and Molina et al. [228]. All of these data were collected in N<sub>2</sub> bath gas, except for several points from Lee et al. [198] collected in O<sub>2</sub>.

The high-pressure-limit recommendation is based on the RRKM calculations of Smith and Golden [133]. There are several pressure-dependent data sets in the literature, such as Percival et al. [266], Handwerk and Zellner [139], Dasch et al. [90] and Cox and Lewis [80]; however, they are too disparate to extract unambiguous values. These data are all reproduced within two-sigma error limits by the current recommendation. However, the value of m = 1.9 is somewhat large. If m = 1 is chosen the computed rate constant is lower by about 20% at 180K and pressures above 500 torr. (Table: 06-2, Note: 06-2) [Back to table](#)

- F9. OClO + NO<sub>3</sub>. Friedl et al. [121], studied this system at 1 ≤ P/Torr ≤ 5 for helium and 220 ≤ T/K ≤ 298. They deduced values for the rate constant consistent with their data of k<sub>0</sub> ≈ 10<sup>-31</sup> and k<sub>∞</sub> ≈ 10<sup>-11</sup>. They also suggest a value for the equilibrium constant: K/cm<sup>3</sup> molecule<sup>-1</sup> = 1 × 10<sup>-28</sup> exp (9300/T). Boyd et al. [39] raised the question of possible heterogeneous effects in this system. Parthiban et al. [263] in a theoretical study, support the finding of Friedl et al. [121] of the species O<sub>2</sub>ClONO<sub>2</sub>, but suggest a very different equilibrium constant. (See Table 3-1). (Table: 94-26, Note: 06-2) [Back to table](#)
- F10. ClO + ClO. The recommendation is based on a simultaneous fit to data from Bloss et al. (183–245 K) [38], (which supersedes earlier work of Sander et al. (194–247 K) [290]), Nickolaisen et al. (260–390 K) [236] and Troler et al. (200–263 K) [327]. The latter data have been corrected for the effect of Cl<sub>2</sub> as third body, as suggested by Nickolaisen et al. With this adjustment all the data are in reasonable agreement. Error limits are from the statistical fit. Golden [130] has performed RRKM and master equation calculations using the potential energy surface in Zhu and Lin [373] and concluded that while a channel to form ClOClO might obtain, the best representation of the data remains as recommended in JPL 02-25. [The value of m = 2.4 is somewhat high, but since the recommended parameters fit data taken over the range of pressure and temperature obtaining in the atmosphere, they have not been altered.] The k<sub>0</sub> value for N<sub>2</sub> is not in accord with a Patrick and Golden-type calculation [265]. This may be due to uncertainty in the ClOClO thermochemistry, which is based on the equilibrium constants reported by Nickolaisen et al. and Cox and Hayman [79] (See Table 3.). It has been suggested [326] that the “radical-complex” mechanism may apply here. Other previous rate constant measurements, such as those of Hayman et al. [142], Cox and Derwent [77], Basco and Hunt [23], Walker

[339], and Johnston et al. [164], range from  $1-5 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$ , with  $\text{N}_2$  or  $\text{O}_2$  as third bodies. The major dimerization product is chlorine peroxide (Birk et al. [34], DeMore and Tschuikow-Roux [96], Slanina and Uhlik [310], Stanton et al. [317] and Lee et al. [197]). (Table: 02-25, Note: 06-2) [Back to table](#)

- F11.  $\text{ClO} + \text{OCIO}$ . Data are from Burkholder et al. [49], who measured the rate constant in  $\text{N}_2$  at  $200 \leq T/\text{K} \leq 260$  and densities from  $(1.1-10.9) \times 10^{18} \text{ molecules cm}^{-3}$ . They also measured the equilibrium constant. (See Table 3) Parr et al. [261] also report a value for the rate constant in reasonable agreement with the recommendation. Zhu and Lin [375] report an ab initio study of this system. Their parameters are somewhat different from those herein, but they fit the data equally well. Green et al. [134] report a value in He that is consistent with the values recommended herein. (Table: 06-2, Note: 06-2) [Back to table](#)
- F12.  $\text{O} + \text{OCIO}$ . The recommendation is based on data of Colussi et al. [72] and Colussi [71], who measured the pressure dependence between 248 and 312 K in Ar. They interpret the intercept of their  $k$  vs  $[\text{M}]$  curves as a zero-pressure rate constant of  $(1.6 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with a negative activation energy corresponding to a chemical activation channel producing  $\text{ClO} + \text{O}_2$ . A low pressure study by Gleason et al. [129], as well as a theoretical study by Zhu and Lin [374], suggests a direct abstraction with a positive activation energy. (Zhu and Lin [374] point out that sym- $\text{ClO}_3$  has a positive barrier for dissociation to  $\text{ClO} + \text{O}_2$ .) The recommended values are fit to the data after subtracting the abstraction channel. See Table 1-1. (Table: 06-2, Note: 06-2) [Back to table](#)
- F13.  $\text{CH}_2\text{Cl} + \text{O}_2$ . Measured by Fenter et al. [112] over the range  $298 \leq T/\text{K} \leq 448$  and  $1 \leq P/\text{Torr} \leq 760$  in nitrogen. Two different techniques were employed: laser photolysis/photoionization mass spectrometry in the range 1–10 Torr and laser photolysis/UV absorption for the range 20–760 Torr. A study by Bilde et al. [33] in  $\text{N}_2$  relative to the reaction  $\text{CH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + \text{Cl}$  is in excellent agreement. Error limits transposed to the current format. (Table: 06-2, Note: 06-2) [Back to table](#)
- F14.  $\text{CHCl}_2 + \text{O}_2$ . Measured by Fenter et al. [112] over the range  $298 \leq T/\text{K} \leq 383$  and  $1 \leq P/\text{Torr} \leq 760$  in nitrogen. Two different techniques were employed: laser photolysis/photoionization mass spectrometry in the range 1–10 Torr and laser photolysis/UV absorption for the range 20–760 Torr. A study by Nottingham et al. [244], in He, is in agreement. Error limits transposed to the current format. [Back to table](#)
- F15.  $\text{CCl}_3 + \text{O}_2$ . The recommendation incorporates studies by Fenter et al. [113], Danis et al. [89] and Luther et al. [210]. (Their data above 100 bar are affected by diffusion.) Experimental data of Ryan and Plumb [288] have been considered in the evaluation. A study by Nottingham et al. [244], in He, is in agreement. Forst and Caralp [116] have examined this reaction theoretically. A Patrick and Golden-type calculation using the thermochemistry of Russell et al. [286] yields  $k_0^{300} = 1.5 \times 10^{-30}$ , with  $\beta = 0.3$ . A value of  $k_\infty^{300} = 5 \times 10^{-12}$  has been reported by Cooper et al. [74]. The value of the rate constants recommended here vary slightly from those of Luther et al., (who report  $k_\infty^{300} = 5.2 \times 10^{-12}$ ;  $m = 1.4$  and  $k_0^{300} = 1.5 \times 10^{-30}$ ;  $n = -6.3$ ;  $F_c = 0.35 \times (T/300)^{-0.35}$  using the IUPAC formula) but yield an overall rate constant within their error limits. (Table: 06-2, Note: 06-2) [Back to table](#)
- F16.  $\text{CFCl}_2 + \text{O}_2$ . Values for both low- and high-pressure limits at 300 K are from Caralp and Lesclaux [56]. Forst and Caralp [116] have examined this reaction theoretically. Temperature dependences are rough estimates based on their calculations and similar reactions. (Table: 06-2, Note: 06-2) [Back to table](#)
- F17.  $\text{CF}_2\text{Cl} + \text{O}_2$ . Forst and Caralp [116] have examined this reaction theoretically. Temperature dependences are rough estimates based on their calculations and similar reactions. (Table: 06-2, Note: 06-2) [Back to table](#)
- F18.  $\text{CCl}_3\text{O}_2 + \text{NO}_2$ . Statistical fit (constrained to  $m=1$ ) to experiments in  $\text{O}_2$  of Caralp et al. [58], who suggest a somewhat different fitting procedure, but the values recommended here fit the data as well. Destriau and Troe [97] use yet a different fitting procedure that does not represent the data quite as well as that recommended herein. Reverse rate data are given by Köppenastrop and Zabel [183]. (Table: 06-2, Note: 06-2) [Back to table](#)
- F19.  $\text{CFCl}_2\text{O}_2 + \text{NO}_2$ . Statistical fit to experiments in  $\text{O}_2$  of Caralp et al. [58] with constraint that  $m=1$ . Caralp et al. [58] suggest a different fitting procedure, but the values recommended here fit the data as well. Destriau and Troe [97] use yet a different fitting procedure that does not represent the data quite as well as that recommended herein. Reverse rate data are given by Köppenastrop and Zabel [183]. (Table: 06-2, Note: 06-2) [Back to table](#)
- F20.  $\text{CF}_2\text{ClO}_2 + \text{NO}_2$ . A study by Xiong and Carr [364] of the reverse reaction, combined with the equilibrium constant, which was computed from correcting the study by Wu and Carr [363] of the forward reaction in a bath gas consisting of 80%  $\text{CF}_2\text{ClBr} + 20\% \text{O}_2$  for  $\text{N}_2$  bath gas. (The study by Wu and Carr [363] supersedes the earlier work of Moore and Carr [229].) Xiong and Carr [364] report their parameterization differently than in this recommendation, but the values herein reproduce their results to a few percent. Reverse rate data are

also given by Köppenkastrup and Zabel [183] and in a theoretical study by Forst and Caralp [117]. (Table: 06-2, Note: 06-2) [Back to table](#)

- G1. Br+NO<sub>2</sub>. The recommended values are from a study by Kreutter et al. [184]. They regarded the product as BrNO<sub>2</sub>. Their k<sub>0</sub> value in He agrees with the measurement of Mellouki et al. [222] at 300 K. Broske and Zabel [44] and Orlando and Burkholder [246] have shown that cis-BrONO is the major product in their studies. Orlando and Burkholder [246] suggest that isomerization to BrNO<sub>2</sub> is heterogeneous. Lee [195] calculated structure, frequencies and energetics for BrNO<sub>2</sub>, cis-BrONO and trans-BrONO. A Patrick-and-Golden-type calculation using the Lee [195] results yields k<sub>0</sub>(strong collision) ≈ 1.2, 2.5 and 2.1 in units of 1x10<sup>-31</sup> cm<sup>6</sup> molecule<sup>-2</sup>s<sup>-1</sup> for trans-BrONO, cis-BrONO and BrNO<sub>2</sub>, respectively. The sum, 5.9x10<sup>-31</sup>, multiplied by a collision efficiency in N<sub>2</sub> of 0.3 is a factor of about 2.5 lower than the observed k<sub>0</sub> value. Also, the relative yield of BrNO<sub>2</sub> is somewhat too high since Orlando and Burkholder [246] measure BrONO > 75%. Kreutter et al. [184] report an equilibrium constant, which, if cis-BrONO is assumed to be the product, suggests bond strengths for the BrONO compounds that are about 4 kcal mole<sup>-1</sup> higher than the Lee [195] calculation. Computing k<sub>0</sub> with these new values yields k<sub>0</sub> ≈ 4.5 and 6.4 in units of 1x10<sup>-31</sup> for trans-BrONO and cis-BrONO respectively. When the sum of the rate constants for the three channels is multiplied by the collision efficiency (0.3), the result is 3.9E-31 and the yield of BrONO is 85%. (Table: 06-2, Note: 06-2) [Back to table](#)
- G2. BrO + NO<sub>2</sub>. Values from a study by Thorn et al. [321] that is in excellent agreement with Sander et al. [292] are recommended. Error limits are from a reanalysis of the data. Danis et al. [88] give slightly lower values for the low-pressure-limiting rate constant and a smaller temperature dependence as well. This latter study may be hampered by heterogeneous effects, but can be accommodated within the error limits recommended. A theoretical study by Rayez and Destriau [281] suggests that the bond-dissociation energy in BrONO<sub>2</sub> is 8.5 kcal mol<sup>-1</sup> higher than in ClONO<sub>2</sub>, thus rationalizing the relative values of the low-pressure-limiting rate constants for these two processes. A more detailed theoretical study by Parthiban and Lee [262], as well as a study by Orlando and Tyndall [247], who measured BrONO<sub>2</sub> decomposition and thus an equilibrium constant, both determine only 1.6 kcal mol<sup>-1</sup> for the above difference. A theoretical study by Zou et al. [378] agrees with the latter figure. A Patrick and Golden [265] type calculation, even with the stronger bond of Rayez and Destriau [281] yields a value for the low pressure limiting rate constant that is less than observed. Lessar et al. [200] calculate a potential energy surface for BrOONO. They find that the BrO – ONO bond strength is of the order of 7 kcal mol<sup>-1</sup>, which is too weak to have any effect on the overall rate of BrO + NO<sub>2</sub>. *The temperature dependence of the high pressure rate constant seems large. The data can be fit quite well with k<sub>∞</sub> = 8 × 10<sup>-12</sup>(T/300)<sup>-1</sup>.* (Table: 06-2, Note: 06-2) [Back to table](#)
- H1. I + NO. Evaluation taken from IUPAC [160]. The data are from van den Bergh et al. [332] and Basco and Hunt [22]. Error limits transposed to the current format. The heat of formation of INO is given as 120.0±0.3 kJ/mole by Forte et al. [119]. (Table: 06-2, Note: 06-2) [Back to table](#)
- H2. I + NO<sub>2</sub>. Evaluation taken from IUPAC [160]. The data are from van den Bergh et al. [332], Mellouki et al. [222], Buben et al. [47] and van den Bergh and Troe [333]. IUPAC uses F<sub>c</sub> = 0.63, which is the same as the universal value adopted here of F<sub>c</sub> = 0.6. (No evidence of possible isomers [INO<sub>2</sub> or IONO] is reported.) Error limits transposed to the current format. (Table: 06-2, Note: 06-2) [Back to table](#)
- H3. IO + NO<sub>2</sub>. Data from Daykin and Wine [94], Hölscher and Zellner [150], Allan and Plane [3] and Jenkin and Cox [162]. Two more studies at lower pressures are available, Larin et al. [191], and Maguin et al. [212]. These do not agree very well with the above four studies and have higher experimental errors. The recommended k<sub>0</sub> and k<sub>∞</sub> also agree with a theoretical study by Rayez and Destriau [281]. (Table: 06-2, Note: 06-2) [Back to table](#)
- I1. HS + NO. Data and analysis are from the work of Black et al. [36]. The temperature dependence of k<sub>0</sub> has been adjusted to give a better fit than in JPL 02-25. The temperature dependence of k<sub>∞</sub> has been estimated. (Table: 06-2, Note: 06-2) [Back to table](#)
- I2. CH<sub>3</sub>S + NO. The recommended values are fit to the study by Balla et al. [20]. The temperature range was 295 to 453K and pressures of N<sub>2</sub> from 1.5 to 300 torr. The change in the high pressure limiting rate coefficient and its temperature dependence reflect a better fit to the data. (Table: 06-2, Note: 06-2) [Back to table](#)
- I3. O + SO<sub>2</sub>. Naidoo et al. [233] studied this spin forbidden reaction in Ar over the temperature range 290<T/K<840 and pressure range 100<P/mbar<880. They fit the data very well using the IUPAC [15] format with k<sub>0</sub> = 9.5x10<sup>-23</sup>T<sup>-3</sup>exp(-2400/T) cm<sup>6</sup>molecule<sup>-2</sup>s<sup>-1</sup>, k<sub>∞</sub> = 6.1x10<sup>-13</sup>exp(-850/T) cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> and F<sub>c</sub> = 0.558exp(-T/316)+0.442exp(-T/7442). The recommended values transpose the rate constants to the form used in this evaluation and are used with the standard value of F<sub>c</sub> = 0.6. These parameters don't fit the higher temperatures as well as the values derived by Naidoo et al. [233], missing the values at 840K by about 50% and those at 699K by about 20%. Values at 289, 399 and 581K are fit quite well and are adequate for atmospheric



conditions. Earlier values are reported by Atkinson and Pitts [18] and Müller et al. [232] (Table: 06-2, Note: 06-2) [Back to table](#)

14. OH + SO<sub>2</sub>. Values of the rate constant as a function of pressure and temperature are from Blitz et al. [37]. They used a five parameter fit to the data, allowing Fc to be temperature dependent. The values of k<sub>0</sub> and k<sub>∞</sub> have been adjusted in the Table to accommodate Fc = 0.6. Blitz et al. [37] determined the high pressure limit from the reaction of OH(v=1) with SO<sub>2</sub>. Their low pressure value was taken by re-evaluating the data of Wine et al. [359] in various bath gases at pressures up to 150 torr and temperatures between 260 K and 420 K, through the use of a master equation. The data of Paraskevopoulos et al. [260] in the same pressure range, is equally well fit. Lower pressure data from at 298 K from Leu [201] and Lee et al. [199] are well accommodated by the recommendation herein. Earlier data listed in Baulch et al. [27], Baulch et al. [26] and Atkinson et al. [15] are noted. Blitz et al [37] have calculated the entropy and measured a third law heat of formation for HOSO<sub>2</sub> (373±6kJ/mol). See also Li and McKee [203]. (Table: 06-2, Note: 06-2) [Back to table](#)
15. CH<sub>3</sub>SCH<sub>2</sub> + O<sub>2</sub>. Wallington et al. [346] have employed a pulse radiolysis technique, obtaining k = (5.7 ± 0.4) × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> in 992 mbar of SF<sub>6</sub> at room temperature. A theoretical study by Resende and De Almeida [282] yields a heat of formation of the product, CH<sub>3</sub>SCH<sub>2</sub>O<sub>2</sub>, as 6.51 kcal mol<sup>-1</sup>. (Table: 94-26, Note: 06-2) [Back to table](#)
16. SO<sub>3</sub> + NH<sub>3</sub>. Recommendation is from Lovejoy [208]. This study covered 20-80 Torr from 280 – 340 K. An earlier study by Lovejoy and Hanson [209], who studied this reaction from 10–400 Torr N<sub>2</sub> at 295 K is in agreement. Lovejoy and Hanson [209] observed that any incipient adduct rapidly becomes sulfamic acid (H<sub>3</sub>NSO<sub>3</sub>) which clusters efficiently with itself and sulfuric acid. The observed sulfamic acid dimerization rate constant exceeds 5 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Measurements of Shen et al. [305] made at 1–2 Torr He are much higher than those of Lovejoy and Hanson [209] or Lovejoy [208]. Error limits have been adjusted to take into account the fact that the exponent of the temperature dependence of the low pressure rate constant is unusually large. Lovejoy [208] also reports an equilibrium constant and heat of formation of sulfamic acid of -24±1 kcal mol<sup>-1</sup>. (Table: 06-2, Note: 06-2) [Back to table](#)
17. HO + CS<sub>2</sub>. The data is from Hynes et al. [reaction 38 in Table 3-1] and Murrells et al. [reaction 32 in Table 3-1]. The value m = 1 is constrained. The adduct reacts slowly with O<sub>2</sub>. (See Table 1-1.) (Table: 06-2, Note: 06-2) [Back to table](#)
18. Cl + CS<sub>2</sub>. The data is from Nicovich et al. [239]. Wallington et al. [341] have also studied this system. The value m = 0 is constrained. Nicovich et al. [239] confirm that the reaction proceeds via reversible adduct formation as suggested by Martin et al. [216]. The much larger rate constant values determined by Martin et al. may possibly be attributed to reactive impurities in the CS<sub>2</sub> sample. Nicovich et al. set an upper limit on the rate constant for the adduct (CS<sub>2</sub>Cl) reacting with O<sub>2</sub> of 2.5 × 10<sup>-16</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature. Wang and Phillips [351] have performed a theoretical study of the adduct. (Table: 06-2, Note: 06-2) [Back to table](#)
19. Cl + (CH<sub>3</sub>)<sub>2</sub>S. If the HCl yield at 297K from Stickel et al. [318] is used as a measure of the abstraction reaction, the rate constant would be 1.64 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Using this value the complete data set from Stickel et al. [318] can be fit with form used in Table 2 with the addition of a term for the abstraction in the form k<sub>abs</sub> = 1.64 × 10<sup>-10</sup> \* (T/300)<sup>a</sup>. The value of “a” obtained in this manner is almost zero, so the data is fit with: k<sub>0</sub> = 4 × 10<sup>-28</sup> \* (T/300)<sup>-7.0</sup> and k<sub>∞</sub> = 2 × 10<sup>-10</sup> (T/300)<sup>-1</sup> along with the temperature independent value of k<sub>abs</sub>. On the other hand, a study by Diaz-de-Mera et al. [99] performed in the temperature range 259 < T/K < 364 and in helium at pressures of 0.5 < p/torr < 1 reports a value k<sub>abs</sub> = (2.0 ± 1.2) × 10<sup>-10</sup> exp[-(332 ± 173)/T], which yields 6.6 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature. Several studies, both experimental by Urbanski and Wine [330] and theoretical by Resende and De Almeida [283] make it clear that at higher pressures an adduct Cl-S(CH<sub>3</sub>)<sub>2</sub> is formed and this adduct does not yield CH<sub>3</sub> radicals or the products of the abstraction pathway. (Table: 06-2, Note: 06-2) [Back to table](#)
110. Br + (CH<sub>3</sub>)<sub>2</sub>S. Wine et al. [358] data for the adduct formation in N<sub>2</sub> at 25 < P/torr < 600 and 263 < T/K < 310 can be evaluated in the NASA format. This leads to the values recommended. Studies by Ingham et al. [159] and Nakano et al. [234] are in agreement. Nakano et al. [234] is also in agreement with the value of the equilibrium constant. However, Maurer et al. [218] find a value at 300K and 1 bar total pressure of a mixture of 5% O<sub>2</sub> and 95% N<sub>2</sub>, only 2% as high as the value computed from the recommended parameters. This latter value is supported by Ballesteros et al. [21]. (Table: 06-2, Note: 06-2) [Back to table](#)
- J1. Na + O<sub>2</sub>. A study by Plane and Rajasekhar [272] finds k<sub>0</sub> = (2.9 ± 0.7) × 10<sup>-30</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> at 300 K with n = 1.30 ± .04. They also estimate k<sub>∞</sub> to be about 6 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> with a small positive temperature dependence. Another study by Helmer and Plane [143] yields k<sub>0</sub> = (3.1 ± 0.2) × 10<sup>-30</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> at 300 K with n = 1.52 ± 0.27. The recommended values are taken from these studies. They are consistent with values measured by Marshall et al. [215] at 600 K and those measured by Vinckier et al. [336] at higher

temperature. The  $k_0$  value is about 60% higher than that of Silver et al. [307]. (Table: 06-2, Note: 06-2) [Back to table](#)

- J2.  $\text{NaO} + \text{O}_2$ . Ager and Howard [1] have measured the low- pressure limit at room temperature in several bath gases. Their value in  $\text{N}_2$  is used in the recommendation. They performed a Troe calculation, as per Patrick and Golden [265], to obtain collision efficiency and temperature dependence. They obtained a high-pressure-limit rate constant by use of a simple model. The temperature dependence is estimated. (Table: 06-2, Note: 06-2) [Back to table](#)
- J3.  $\text{NaO} + \text{CO}_2$ . Ager and Howard [1] have measured the rate constant for this process in the “fall-off” regime. Their lowest pressures are very close to the low-pressure limit. The temperature dependence is an estimate. Ager and Howard calculate the high-pressure rate constant from a simple model. (Table: 06-2, Note: 06-2) [Back to table](#)
- J4.  $\text{NaOH} + \text{CO}_2$ . Ager and Howard [2] have measured the low-pressure-limiting rate constant. The temperature dependence is an estimate. Ager and Howard have calculated the high-pressure limit using a simple model. (Table: 06-2, Note: 06-2) [Back to table](#)

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